UNIVERSITI PUTRA MALAYSIA

SYNTHESIS BY PRECIPITATION AND CHARACTERISATION OF ANTIMONY TETRAOXIDE

IZHAM BIN SAIMAN.

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MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

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By

MOHD IZHAM BIN SAIMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

April 2006

Especially Dedicated To
My beloved wife,
Siti Normadeha bt. Mohammad Amin
My newborn baby,
Nur Damia Safiyah bt. Mohd Izham
and my family

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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MOHD IZHAM BIN SAIMAN

April 2006

Chairman: Associate Professor Mohd Basyaruddin bin Abdul Rahman, PhD

Faculty : Science

Antimony oxide has found application in various area including clarification, pigment, material synthesis and catalyst. This study investigated the influence of synthesis parameters (precipitating agent and solvent) on the formation of antimony oxide powder. Characterizations of the samples were carried out by Thermogravimetry Analysis (TGA), X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, BET surface area measurement and Scanning Electron Microscopy (SEM).

Investigations on the influence of the type of precipitating agents (NaOH and NH_4OH), on the formation of antimony oxide revealed that α-Sb_2O_4 was produced after the precursors were calcined. The precursors were a mixture of $Sb_4O_5Cl_2$ and Sb_2O_3 phase when precipitated with NaOH but only Sb_2O_3 phase when precipitated with NH_4OH. By varying the two precipitation agent, NH_4OH

solution gave better surface areas and fine morphologies for the samples compared to NaOH solution.

On the influence of solvent, ethanol gave full reflection of Sb_2O_3 and different structure phase before calcination process. No phase of the antimony oxy chloride was obtained for these samples. After calcined process, all samples gave full reflection of the α-Sb_2O_4. Usage of the NaOH as a precipitating agent gave higher surface area compared to NH_4OH samples.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS MELALUI PEMENDAKAN DAN PENCIRIAN ANTIMONI TETRAOKSIDA

Oleh

MOHD IZHAM BIN SAIMAN

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Pengerusi: Profesor Madya Mohd Basyaruddin bin Abdul Rahman, PhD.

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Antimoni oksida mempunyai aplikasi dalam pelbagai bidang termasuk klarifikasian, pigmen, sintesis bahan dan pemangkinan. Kajian ini menyelidik kesan pelbagai parameter sintesis (agen pemendakan dan pelarut) ke atas pembentukan serbuk antimoni oksida. Pencirian telah dilakukan dengan mengunakan analisis termo gravitimetri (TGA), teknik Pembelauan Sinar (XRD), Spektroskopi Inframerah (FTIR), Pengukuran Luas Permukaan BET, dan Mikroskopi Pengimbas Elektron (SEM).

Kajian ke atas kesan beberapa jenis agen pemendakan (NaOH dan NH_4OH) ke atas pembentukan antimoni oksida membuktikan bahawa α-Sb_2O_4 terhasil selepas bahan pemula dikalsin. Bahan pemula adalah campuran fasa $Sb_4O_5Cl_2$ dan Sb_2O_3 apabila dimendakkan dengan NaOH tetapi hanya Sb_2O_3 apabila dimendakkan dengan larutan NH_4OH. Dengan membezakan kedua-dua agen

pemendakan, larutan NH_4OH menberikan luas permukaan dan morfologi yang lebih baik berbanding sampel menggunakan larutan NaOH bagi sampel tersebut.

Berdasarkan kesan pelarut, etanol telah memberikan refleksi yang penuh bagi Sb_2O_3 tetapi berbeza fasa sebelum proses kalsin. Tidak terdapat fasa antimoni oksiklorida dikesan pada sampel ini. Semua sampel telah menunjukkan refleksi yang penuh bagi α-Sb_2O_4 selepas proses pengkalsinan. Penggunaan NaOH sebagai agen pemendakan telah memberikan luas permukaan yang lebih tinggi berbanding sampel menggunakan larutan NH_4OH.

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In The Name of ALLAH S.W.T., the Most Merciful, Most Compassionate

For The Blessing and Strength

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I certify that an Examination Committee has met on 21st April 2006 to conduct the final examination of Mohd Izham bin Saiman on his Master of Science thesis entitled "Synthesis by Precipitation and Characterisation of Antimony Tetraoxide" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirements for the degree of Master of Science. The members of Supervisory Committee are as follows:

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Date: 10 AUG 2006

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

MOHD IZHAM BIN SAIMAN

Date: 4th July 2006

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

BET	Brunauer-Emmet-Teller
DTA	Differential Thermal Analysis
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full-Width at Half Maximum
JCPDS	Joint Committee on Powder Diffraction Standards
$SbNa_{0.5}$	The antimony oxide sample using 0.5 M of NaOH solution
$SbNa_{1.0}$	The antimony oxide sample using 1.0 M of NaOH solution
$SbNa_{2.0}$	The antimony oxide sample using 2.0 M of NaOH solution
$SbNa_{3.0}$	The antimony oxide sample using 3.0 M of NaOH solution
$SbNH_{0.5}$	The antimony oxide sample using 0.5 M of NH_4OH solution
$SbNH_{1.0}$	The antimony oxide sample using 1.0 M of NH_4OH solution
$SbNH_{2.0}$	The antimony oxide sample using 2.0 M of NH_4OH solution
$SbNH_{3.0}$	The antimony oxide sample using 3.0 M of NH_4OH solution
$SbetNa_{0.5}$	The antimony oxide sample using ethanol solvent and 0.5 M of NaOH solution
$SbetNa_{1.0}$	The antimony oxide sample using ethanol solvent and 1.0 M of NaOH solution
$SbetNa_{2.0}$	The antimony oxide sample using ethanol solvent and 2.0 M of NaOH solution
$SbetNa_{3.0}$	The antimony oxide sample using ethanol solvent and 3.0 M of NaOH solution
$SbetNH_{0.5}$	The antimony oxide sample using ethanol solvent and 0.5

	M of NH_4OH solution
$SbetNH_{1.0}$	The antimony oxide sample using ethanol solvent and 1.0 M of NH_4OH solution
$SbetNH_{2.0}$	The antimony oxide sample using ethanol solvent and 2.0 M of NH_4OH solution
$SbetNH_{3.0}$	The antimony oxide sample using ethanol solvent and 3.0 M of NH_4OH solution
SEM	Scanning Electron Microscopy
TG	Thermogravimetry
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Antimony Oxides

Antimony oxides are known to exist in several different compositions and displayed polymorphism. The two common forms of Sb_2O_3 are the cubic phase senarmontite and orthorhombic phase valentinite. The polymorphic forms of Sb_2O_4 are the orthorhombic α phase (cervantite) and a high-temperature monoclinic β phase [1]. Antimonic acid can be described as $Sb_2O_5.XH_2O$, its dehydration and thermal decomposition product being Sb_6O_{13}, i.e., $Sb_2O_{4.35}$; further heating of Sb_6O_{13} yields Sb_2O_4 as the final composition [2].

1.2 Antimony Trioxide, Sb_2O_3

Antimony trioxide can adopt two crystal structures, both which are stable at room temperature [1]. Cubic Sb_2O_3 (senarmontite) consists of Sb_4O_6 units, which can exist as molecules in the gas phase; orthorhombic Sb_2O_3 (valentinite) has a layered structure, in which long chains (each "link" contains three O^{2-} ions and shares four Sb^{3+} ions) are held together by weak Sb-O interactions [3]. The idealised geometry of the Sb^{III}

coordination can be described as a deformed tetrahedron with the oxygen at three corners and the lone electronic pair of antimony at the fourth corner (Figure 1.1).

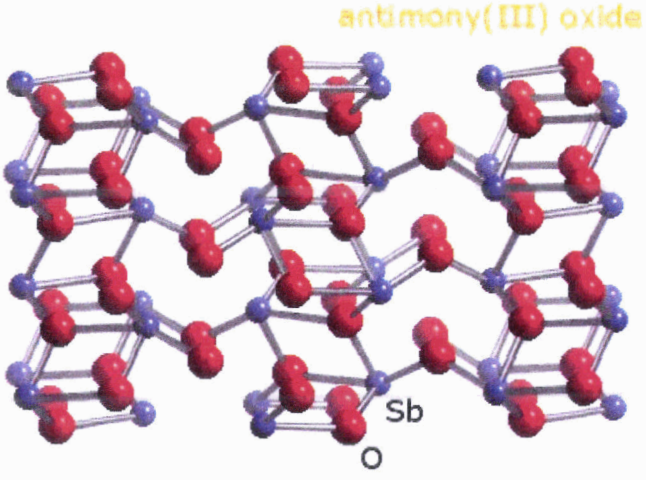

Figure 1.1: The orientation structure of antimony trioxide, Sb_2O_3 [4]

Commercial samples of unspecified Sb_2O_3 may contain both allotropes, but their separation is not considered essential prior to the preparation of mixed-metal oxide catalysts.

Table 1.1 showed that when senarmontite is heated in air at 293 K/min, it was detected that volatilization of Sb_2O_3 and oxidation to Sb_2O_4 occurred simultaneously. A total of about 21% weight loss was observed between 773 and 933 K [1].

Table 1.1: Summary of Thermal Analysis Results by Cody *et al.* [1]

Identification[a]	Heating rate K/min	Atmosphere at 100 cm^3/min	Reaction temp, K	Residue	Condensate
Sb_2O_3 Sen	293	air	773-913 vol. of Sen.	α-Sb_2O_4,933-1208 K	Sen.[b] above 1223 K
Sb_2O_3 Sen	293	N_2	773-1023 vol of Sen.	-	-
Sb_2O_3 Val	293	air	773-833 vol of Val.	α-Sb_2O_4,843-1208 K	Sen. above 1223 K
Sb_2O_3 Val	293	N_2	773-1063 vol of Val.	-	Sen.
α-Sb_2O_4	293	air	1050-onset[c] of vol	mostly α-Sb_2O_4; minor β-Sb_2O_4	Sen.[b] at 1468 K
α-Sb_2O_4	293	N_2	1273-onset[c] of vol	α-Sb_2O_4	Sen.[b] at 1373 K
β-Sb_2O_4	293	air	1323-onset of vol	β-Sb_2O_4 at 1473 K	Sen.[b] at 1473 K
β-Sb_2O_4	293	N_2	1243-onset of vol	β-Sb_2O_4 at 1403 K	Sen. at 1403 K
$Sb_2O_5.XH_20$	323	air	923-1123 Sb_6O_{13}	α-Sb_2O_4,1163-1243 K	Sen. above 1243 K
$Sb_2O_5.XH_20$	323	N_2	923-1173 Sb_6O_{13}	α-Sb_2O_4, 1223-onset of vol	Sen. above 1223 K

[a]Key: Sen.=senarmontite, Val.=valentinite, vol=volatilization. [b]Senarmontite found in cooler region of furnace, valentinite in the moderate temperature region and α-Sb_2O_4 in the hooter temperature zone. [c]Varies according to method of preparation and atmosphere employed